

PHASE TRANSITION IN $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$

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In $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$ crystal (containing Mn(II) in the ratio of Zn(II) to Mn(II) 100:1 and 10:1) a phase transition connected with the occupation of two inequivalent octahedra complexes GeF_6^{2-} positions was discovered and studied by means of ESR. The phase transition has a hysteresis nature. Transition temperature ranges depend on the concentration of the added ion. The origins of these phenomena are discussed.

The crystals $\text{ABF}_6 \cdot 6\text{H}_2\text{O}$ form an interesting class of compounds, in which near regular $[\text{A}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{BF}_6]^{2-}$ octahedra are packed in a trigonal distorted CsCl-like structure. A number of systems of this type of structure are known at present, including $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ of symmetry $\text{R}\bar{3}$ [1], or $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$, of symmetry $\text{R}\bar{3}\text{m}$ [2]. Both types of crystals contain one formula per unit cell. The electron spin resonance (ESR) spectrum corresponding to this type of structure has been observed in nickel and zinc fluorosilicates [3,4] over a wide temperature range. However, in ferrous fluosilicate (with Ni^{2+}) at 4.2 K a spectrum, corresponding to six nonequivalent positions of the added ion, was discovered [5]. Recently, Rubins reported [6] the ESR observation of the transition from an orthorhombic structure with six magnetic centers to a trigonal structure with one centre at 182 ± 2 K in $\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$.

We have discovered a structural phase transition in another crystal of the aforementioned class, in $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$ and in this letter the results of its investigation are given.

The space group of the symmetry of zinc fluorogermanate is $\text{R}\bar{3}$ [7]. The investigation of the temperature dependence of the ESR spectrum of certain iron group ions in $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$ have shown that at $T \approx 200$ K the symmetry of the crystalline field acting

on the impurities changes rapidly. In order to make a more detailed investigation of the observed phenomena we use Mn^{2+} as an admixture.

At 300 K the ESR spectrum of Mn^{2+} in $(\text{Mn}_x \text{Zn}_{1-x}) \text{GeF}_6 \cdot 6\text{H}_2\text{O}$ (here $x = 0.01; 0.1$; according to synthesis) have an axial symmetry with the Z axis directed along the L_3 axis of the crystal. At 77 K, the ESR spectrum is due to six nonequivalent positions of the water molecules in the octahedra, the Z axes of which make an angle of $\approx 10^\circ$ with L_3 . The ESR spectra of the different centres have an equal intensity in pairs. The intensity ratio for different pairs differs from 1 irregularly in the various crystals. The X and Y axes of the spectrum are situated symmetrically about $\{1\bar{1}0\}$, and the projection of the X axis on the (111) plane of one of the octahedra coincides with the projection of the Y axes of the other, and vice versa. This picture repeats over intervals of $33^\circ, 27^\circ, 33^\circ, \dots$ etcetera. This is explained in fig. 1, in which the projection of the g tensor axes for two centres of equal intensity on the (111) plane is presented.

The observed ESR line positions are fitted to the spin hamiltonian:

$$\begin{aligned} \hat{\mathcal{H}} = & g\beta H \hat{S} + D[\hat{S}_Z^2 - \frac{1}{3}S(S+1)] + E(\hat{S}_X^2 - \hat{S}_Y^2) - \hat{F}(a) \\ & + A\hat{S}_Z\hat{I}_Z + B(\hat{S}_X\hat{I}_X + \hat{S}_Y\hat{I}_Y), \end{aligned} \quad (1)$$

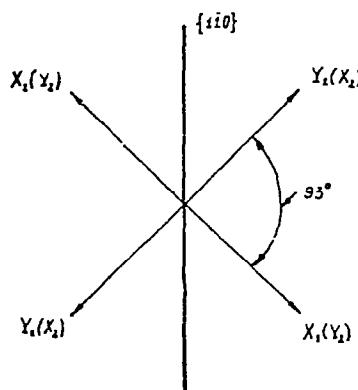


Fig. 1. The projection of the g tensor axes for two spectra of equal intensity on the (111) plane. The full picture can be obtained by a rotation of $\pm 120^\circ$ about L_3 (the L_3 axis passes through the origin of coordinates perpendicular to the plane of the figure).

with $S = 5/2, I = 5/2$. The hamiltonian parameters determined for the various temperatures are given in table 1. The signs of A, B, α and D are obtained by a procedure analogous to that given in ref. [8].

In order to investigate the transition range directly, the temperature dependence of the positions (fig. 1) and intensity (fig. 2) of the low field line of Mn(II) in $(\text{Mn}_{0.01}\text{Zn}_{0.99})\text{GeF}_6 \cdot 6\text{H}_2\text{O}$ at $\Theta = 0^\circ$ was studied (here Θ is the angle between L_3 and the direction of the static external magnetic field). The rate of temperature change was less than $1^\circ/\text{min}$.

From figs. 2 and 3 it is seen how the transformation from the high- to the low-temperature spectrum takes place. It should be noted that 90% of the transition from one spectrum to the other takes place in the temperature range from 190 K to 194 K; however, at the lower as well as at the higher sides of this range one spectrum contains a trace of the other. No other qualitative change in the spectrum is observed during a further temperature decrease from the transition range to 4.2 K, except that the value of D continues to de-

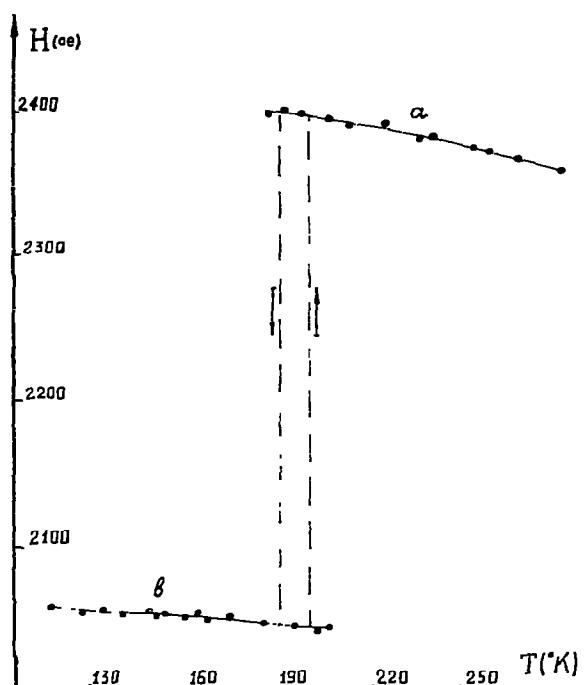


Fig. 2. The temperature dependence of the position of the low field line of Mn(II) in $(\text{Mn}_{0.01}\text{Zn}_{0.99})\text{GeF}_6 \cdot 6\text{H}_2\text{O}$ at $\Theta = 0^\circ$.

crease monotonically.

Heating the sample from 77 K to room temperature transforms the "b" type spectrum to the "a" type, but the transition takes place at higher temperatures (figs. 2 and 3), which means that the transition is hysteresis in nature. The critical temperature regions, in which the transitions are observed, are independent of the rate of temperature change (in the experiments this rate was decreased down to $0.2^\circ/\text{min}$).

The investigation of the phase transition in $(\text{Mn}_{0.1}\text{Zn}_{0.9})\text{GeF}_6 \cdot 6\text{H}_2\text{O}$ has shown that the transition points are shifted about 6° to higher temperatures. The difference between the transition temperatures

Table 1
The ESR spectral parameters of Mn(II) in crystals of $(\text{Mn}_x\text{Zn}_{1-x})\text{GeF}_6 \cdot 6\text{H}_2\text{O}$ (where $x = 0.01, 0.1$)

$T(\text{K})$	$D(\text{Oe})$		$A(\text{Oe})$	$B(\text{Oe})$	g	$a(\text{Oe})$	$E(\text{Oe})$
	$x = 0.01$	$x = 0.1$					
300	-191 ± 1	-192 ± 2	-95 ± 0.5	-95 ± 0.5	2.0010 ± 0.0005	8 ± 1	0
77	-263 ± 3	-265 ± 3	-96 ± 2	-96 ± 2	2.000 ± 0.005	8 ± 2	≈ 50
30	-260 ± 3	-263 ± 3	-96 ± 2	-96 ± 2	2.000 ± 0.005	8 ± 2	≈ 50

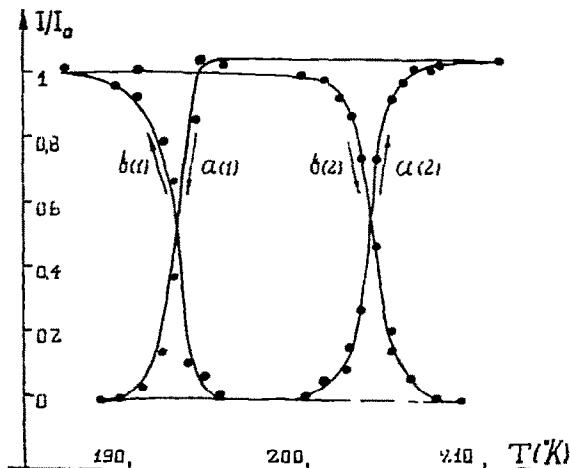


Fig. 3. The temperature dependence of the intensity of the low field line of Mn(II) in $(\text{Mn}_{0.01}\text{Zn}_{0.99})\text{GeF}_6 \cdot 6\text{H}_2\text{O}$ at $\Theta = 0^\circ$. I_0 is the line intensity at $T = 190$ K.

for crystal cooling and heating is approximately equal to that in the $(\text{Mn}_{0.01}\text{Zn}_{0.99})\text{GeF}_6 \cdot 6\text{H}_2\text{O}$ crystal, about 12° .

Thus, during the phase transition, a rapid transformation of the crystal symmetry takes place, which is manifested in the ESR spectrum by the appearance of nonequivalent positions in the octahedra. The angle dependence of the ESR spectra, taking into account the difference in signal intensity, shows that after the phase transition there are three types of crystallites (domains) in the crystal. The crystallites are connected to each other by rotation about L_3 through an angle of 120° . The phase transition hysteresis means that the formation of crystallites (domains) is accompanied by a loss of the crystal integrity. The hysteresis value can serve as a measure of the recrystallization energy.

The configuration of the complexes is also transformed at the phase transition; the axial component of the crystalline field considerably increases, and the symmetry is lowered. The value of the angle α between the central ion and the two water molecules which lie in the plane perpendicular to the threefold axis of the complex $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ before and after the phase transition can be estimated according to ref. [4]. The values of this angle are $\alpha(300\text{ K}) \approx 89^\circ$; $\alpha(77\text{ K}) \approx 88^\circ 30'$. Consequently as a result of the phase transition, the elongation of the water octahedra along the threefold axis increases. At the same time the complex

$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ acquires a rhombic component of the distortion.

The following scheme may be suggested for understanding the nature of the observed phase transition. First of all it will be noted, that in certain crystals of the class under investigation the real structure proves to be more complicated. An X-ray diffraction study showed [1], that, in $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$, $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$, $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$, there is disorder caused by two non-equivalent positions of fluorine octahedra unrelated by any symmetry elements and with unequal occupancy. In particular, the ratio of the population of these two positions equals 33:67 in $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ crystal.

The study of $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$ crystal with a small admixture of ferric ions (Fe^{3+} ions replaced Ge^{4+} ions in fluorine octahedra) shows, that in this crystal there also exist two positions of the GeF_6^{2-} octahedra, distinguished by angular displacement about the trigonal axis. The direct measurements of the temperature dependence of the ESR signal intensity of Fe^{3+} showed that the ratio of the population of the two positions of the fluorine octahedra at room temperature equals 10:13 and tends to unity with decreasing temperature.

The disorder of the crystal is probably caused by the existence of spacial positions for its fragments, in which the energy of their interaction with the surrounding structural units (for example, through hydrogen bonds, as in our case) is slightly different. The difference in the energy of the states is not constant with temperature. As a matter of fact, the linear dimensions of the crystal change considerably with temperature, more so in those directions in which neighbours are moved over greater distances. If the energy difference between the octahedra occupying different positions decreases to zero at a certain temperature, a phase transition is possible in the crystal, according to Landau's theory [10]. Just such a situation is realized in zinc fluorogermainate. Within this model, the absence or presence of a phase transition in crystals of $\text{ABF}_6 \cdot 6\text{H}_2\text{O}$ can be understood.

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